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PROCEEDINGS OF THE SOLVENT REACTIVITY CONFERENCE

Basil Dimitriades

Battelle Columbus Laboratories

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16. ABSTRACT

The concept of photochemical reactivity and its present use in solvent emissions control strategies was reexamined for validity, utility, and desirability. Such reexamination was dictated by recent developments, including new experimental evidence on reactivity of organics and the realization that existing reactivity-related regulations are inconsistent among themselves. It was generally agreed that solvents and other stationary source emissions must be controlled and that use of reactivity criteria on such control is, in principal, sound. EPA offered comments suggesting that the recently verified pollutant transport phenomena would tend to make Appendix B-type regulations more effective relative to the widely used Rule 66 regulation. Another consequence of pollutant transport is that the relatively unreactive organics are induced to form as much oxidant as the reactive ones. Therefore, an appropriate reactivity classification of organics should be based on considerations related to pollution problems caused both within a region and in the downwind areas.

PRICES SUBJECT TO CHANGE

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PROCEEDINGS OF THE SOLVENT REACTIVITY CONFERENCE

Atmospheric Chemistry and Physics Branch
Chemistry and Physics Laboratory

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MORNING SESSION

1. Opening Remarks -- B. Dimitriades, EPA

Dr. Dimitriades extended a welcome to all conference attendants and spoke briefly on the background activity that culminated in the conference.

Staff members of the Chemistry and Physics Laboratory of EPA's Office of Research and Development have been thinking about the problem of solvent emissions and about the possibility and desirability of using reactivity in the control of such emissions. Such concern was instigated by two developments: (a) Recent smog chamber studies suggested that the reactivity classification of organics in the widely used Los-Angeles-County-Rule 66 is incomplete and at points wrong. (b) It was realized that reactivity criteria were not used consistently in existing EPA regulations--such an inconsistency being in principle at least, undesirable. With these developments in mind, an EPA committee of Solvent Reactivity Experts was established and began having conversations with the private sector for the purpose of exploring some relevant questions on the subject of reactivity and its application in solvent emissions control.

The first conclusion reached from these conversations was that EPA should take a close look at whatever data were available on reactivity of organics and, based on such data, attempt to classify organics into reactivity classes more correctly than was done previously. This was done in 1973 and results were described in a first-draft document that was circulated and reviewed extensively. That document also included a discussion of possible methods by which reactivity criteria could be applied in control, as well as a discussion of associated problems and research needs. For a period of several months following the circulation of the document, response was received covering viewpoints from the entire technical community in the country; that is, from federal and state government, private industry and trade associations, and academic institutions. Such response ranged widely, from severe criticism to enthusiastic endorsement. Some of the criticism was judged to be unjustified. Other criticism, however, was well-taken, and has changed somewhat EPA's thinking and conclusions. Therefore, one of the reasons for EPA's interest in this conference is the desire to take the opportunity to present EPA's thinking on the subject, in the light of the response received thus far.

There have been other developments in the past year that are relevant to and of interest in this conference. Thus, the belief that pollutant transport phenomena are important has become stronger. Also, speculations have been made--speculations unsupported by direct evidence but nevertheless rational--that such transport phenomena reduce the differences in true or effective reactivity among all but a few organics. Linking the reactivity concept with pollutant transport introduces a new perspective that certainly deserves attention.

2. On-Going Research in EPA's Chemistry and Physics Laboratory on Pollutant Transport and Transformation -- A. P. Altshuller, EPA

Dr. Altshuller first offered some comments setting the theme and scope of this conference. He emphasized that:

(a) The validity of the Ox-HC curve used by EPA as the basis for determining control requirements is irrelevant to this conference. The conference is intended to deal with questions of "what to do" and "how we do it", following determination of control requirements-- a determination that may or may not be based on EPA's Ox-HC curve.

(b) Reactivity-based control regulations have been in use and, presumably, have been accepted. Therefore, the question "to use or not to use" reactivity criteria is irrelevant; what is relevant is the question of "whether we should improve, and how to improve regulations."

(c) Deficiencies or gaps in existing knowledge and research needs, while within the scope of the conference, should not be discussed in the context of whether they are prohibitive or not. The question to be emphasized is "what do we do now to improve control regulations with the knowledge we have now."

Following these comments, Dr. Altshuller discussed oxidant transport phenomena and their impact on the oxidant-reactivity of organic substances.

Oxidant as defined in the EPA air quality criteria is the gross oxidant measured by the KI method and corrected for nitrogen dioxide and sulfur dioxide interference. Ozone is the predominant oxidant, but the peroxyacyl nitrates present will contribute somewhat to the total response of a colorimetric oxidant analyzer.

Oxidant formation is particularly sensitive to the ratio of organics(HC) to nitrogen oxides (NO_x) present as reactants in the air. Oxidant does not start forming at measurable concentrations until essentially all of the nitric oxide (NO) present is converted to nitrogen dioxide (NO_2). Reducing the HC-to-NO_x ratio slows down the rate of conversion of NO to NO_2 and the rate of formation of oxidant. The lesser the ability of an organic substance to participate in oxidant formation, the more sensitive it is to a given ratio or nitrogen oxide concentration, and the longer it takes for oxidant to be formed at appreciable levels. However, rather substantial variations in composition of atmospheric organic mixtures toward lower reactivity are necessary in order to reduce oxidant formation significantly. Care is required in interpreting laboratory smog chamber results on single hydrocarbons or simple mixtures since these systems are used primarily to demonstrate maximum ranges of effects of compositional changes.

As discussed above, reduction in the HC-to-NO_x ratio or reduction in the photochemical reactivity by compositional changes slows down rather than eliminates the formation of oxidant. Only a small number

of organic substances have been demonstrated to have negligible ability to participate in oxidant formation. Even paraffinic hydrocarbons such as butanes or pentanes participate in oxidant formation and only a small amount of a more reactive organic, if present, can accelerate oxidant formation appreciably.

These circumstances suggest that changes in reactant ratio or organic composition which can reduce oxidant concentration levels near the origin of high emission loadings may not reduce oxidant further downwind. Therefore, control measures that work to the advantage of the urban area where they are initiated may not be effective 50 of 100 miles downwind. Measurements in the Southern California Air Basin, as well as studies around Houston, in Texas, (conducted by Washington State U.) and in the Midwest (conducted by RTI) indicate that urban plumes containing oxidant at or above the air quality standard can fumigate other urban areas or rural areas well downwind. The range of downwind transport of oxidant in urban plumes is under continuing experimental investigation.

The experimental approach commonly used to develop reactivity scales for organic substances is the use of smog chambers. In most of these studies, a fixed initial concentration of each of a series of organic substances is irradiated using simulated solar radiation with a fixed initial concentration of nitrogen oxide. Such chambers normally are operated as static systems at constant light intensity, temperature, and humidity.

Most of these smog chamber experiments have been conducted at a two-to-one ratio ($HC:NO_x$) of reactants. In dicussing the results of such studies, insufficient emphasis was placed on the arbitrary nature of the choice of a two-to-one ratio of reactants. This selection of ratio would not be important if the oxidant yields and dosages were almost independent of reactant ratio. However, there are "lower" reactivity organic substances, such as n-butane and formaldehyde, which yield little oxidant at lower reactant ratios and large amounts of oxidant at higher reactant ratios. Conversely, many "higher" reactivity substances, such as propylene and m-xylene, yield large amounts of oxidant at lower reactant ratios and smaller amounts of oxidant at higher reactant ratios. In part, this difference results from the slower rate of conversion of NO to NO_2 by "lower" reactivity organic substances, being compensated for at higher reactant ratio by the smaller amounts of NO which are available for conversion to NO_2. At the higher reactant ratios, the "higher" reactivity organics cause a rapid conversion of NO into NO_2 followed by NO_2 consumption which, in turn, causes the production of oxidant to cease. In contrast, the "lower" reactivity organics continue to participate in the generation of ozone over a longer time period, resulting thus in high yields and dosages of oxidant.

Emphasis is being placed on high ratio conditions since these are more likely to be associated with large sources of emissions of

organic solvents, petroleum and petrochemical production and related industrial processes. Plumes associated with such emission conditions may produce oxidant more slowly than automobile exhaust, but over a longer distance and for longer periods of time. Therefore, the substitution of "lower" for "higher" reactivity organic substances may assist the local air pollution situation but may not assist as much in reducing oxidant exposure at downwind locations.

What types of studies can contribute to resolving these problems? Field experiments can be designed to differentiating between anthropogenic and natural causes of oxidant formation. Selection of appropriate sites should assist in differentiating between mobile sources and stationary sources of organic emissions in terms of oxidant formation. Field measurements are urgently needed in which the plumes from large extended individual sources of organic emissions are followed downwind to measure oxidant formation as a function of organic concentration and composition. Such plumes are likely to have higher ratios of organics to nitrogen oxides than do the plumes from high traffic density areas.

Properly designed smog chamber experiments can assist materially. Proper selection of reactant ratios, long irradiation periods, and simulation of atmospheric dilution should provide the conditions to better evaluate the significance of low and high reacitivty organic substances in oxidant formation under transport conditions. Smog chambers also can be used to compare the effect on oxidant formation of changes in reactant ratios with changes in solvent composition.

While speculation may be premature, it is possible that additional studies will indicate that elaborate reactivity scales are unnecessary. The more important differentiation needed is likely not to be between "moderate" and "high" reactivity substances. The important differentiation may be between reactive and essentially unreactive substances. For example, the determination of which paraffinic hydrocarbons can be considered as essentially non-reactive or of low reactivity under a wide range of conditions is of particular importance, since paraffinic hydrocarbons constitute an important group of substances with respect to control of organic emissions from solvent use, petroleum production, refining and marketing (including vapor losses at the wholesale and retain levels of use), and the production of petrochemicals.

Another research tool which should be applied is chemical kinetic modeling. Considerable progress is being made in verifying the applicability of such models with smog chamber experiments. Once verified the kinetic model can be used to supplement experimental results by computing results for conditions not covered by the experimental design. The model should be useful in treating reactivity problems.

In applying the outputs of these several approaches we may find it useful to differentiate between relatively isolated urban areas impacting on lightly populated and vegetated areas downwind compared to closely clustered communities possibly involved in fumigation of each other on a significant number of occasions each year. In the former

case the type of reactivity schemes already developed may continue to be applicable. In the latter cases new approaches may be necessary.

Discussion

Questions were raised from the floor (N. J. Butler, Reynolds Metal Company) regarding the role of natural hydrocarbon emissions in the atmospheric photochemical reaction. Dr. Altshuller responded that EPA is presently conducting field studies directed at these questions. He expressed the viewpoint that a small amount of oxidant, probably no more than 50 parts per billion, may form from natural hydrocarbon. If higher values of oxidant are observed in rural areas, then one needs to ascertain whether an urban plume is contributing to the measured oxidant. Terpenes react very fast and are capable of producing photochemical aerosol. However, there are no indications as yet that terpenes contribute significantly to oxidant formation. Natural hydrocarbons other than terpenes may also have a role; however each case should be looked at individually.

Mr. Lebron (Maryland Bureau of Air Quality) remarked that aerometric data in Baltimore indicated that the level of hydrocarbon had no effect on oxidant level; rather it was the morning NO_x that correlated well with oxidant. Dr. Altshuller responded that he would be reluctant to accept these conclusions. Precursor effects are coupled with several factors and it would be very difficult to statistically delineate such coupling. Further, Washington, D. C. data, examined by EPA, did not seem to lend support to Mr. Lebron's conclusions.

Mr. Zimmt (NPCA) commented that the data that had been accumulated on transport effects had been obtained mostly for reactive hydrocarbon mixtures. There have been no studies on how low reactivity mixtures would react, to substantiate such effects. Dr. Altshuller agreed that there have been no case studies of transport effects for low reactivity mixtures.

In response to questions from the floor, Dr. Altshuller explained that there are studies currently under way dealing with city-countryside interactions. The Washington State University, under EPA contract, and EPA are studying the effect of urban emissions on countryside air quality; also, the Coordinating Research Council has contracted Washington State University to study the effect of natural organic emissions on urban air quality.

3. Emission Trends and Pollutant Transport -- R. E. Neligan, EPA

Mr. Neligan expanded on what Dr. Altshuller discussed concerning long distance transport studies. He discussed in detail a study in the mid-west area of the United Sates. Figure 1 shows the study area. Both ground monitoring stations and aircraft sampling were employed.

Table 1 is a summary of the oxidant concentrations obtained at the four monitoring stations. Figure 2 shows the oxidant aircraft measurement. Table 2 shows the rural ozone measurements.

Mr. Neligan discussed also EPA estimates on the mobile and stationary hydrocarbon emissions for 1970 and 1990 and stressed the growing relative importance of the stationary source emissions in future years. Table 3 shows these values for several U. S. cities. These predictions were based on the equation:

$$(1) \qquad Psc = \frac{(Q_i \times G_f \times R_f)sc}{\sum_{sc} (Q_i \times G_f \times R_f)_{sc}} \times 100$$

Where Psc = percent contribution for source category
Q_i = base year emission inventory - 1970
G_f = growth factor for source category, computed
R_f = Predicted emission reduction factor - 1990

Table 4 gives the ratio of mobile and stationary source emissions for the years 1970 and 1990.

Discussion

Mr. Starke (Shell, Houston) asked whether in long distance transport phenomena natural hydrocarbons might have a greater impact on ozone measured at the monitoring site than the man-made emissions. Mr. Neligan responded that there are several possibilities that would have to be considered. For example, ozone may be transferred down from the stratosphere; also natural hydrocarbons may give rise to ozone in the .02 to .03 ppm range. Adding those two sources together it could produce up to .05 ppm of ozone from natural sources. If higher concentrations of ozone are measured then one must ask where does the ozone come from. Mr. Starke pursued his question further by suggesting that it might be possible that man-made sources contribute, for example, one unit whereas natural sources contribute ten units of ozone. Dr. Altshuller and Dr. Bufalini responded with comments suggesting that the field studies now conducted under EPA sponsorship will look into these possibilities. They suggested specifically that the summer program in the midwest is designed to determine the importance of transport of ozone and ozone precursors. Detailed hydrocarbon analysis as well as ozone and nitrogen oxide measurements will be made at several sampling locations in the midwest. This includes ground and vertical sampling. The detailed hydrocarbon analysis should make it possible to determine the importance of nautral sources of ozone precursors. The area under study will cover Cincinnati, Dayton, Wilmington, Columbus, Canton, and Pittsburgh with several rural sites. Mr. Neligan added, in response to Mr. Patrick's (Union Carbide) question, that in these studies attention will be given to the air circulation patterns in the areas where these measurements will be made.

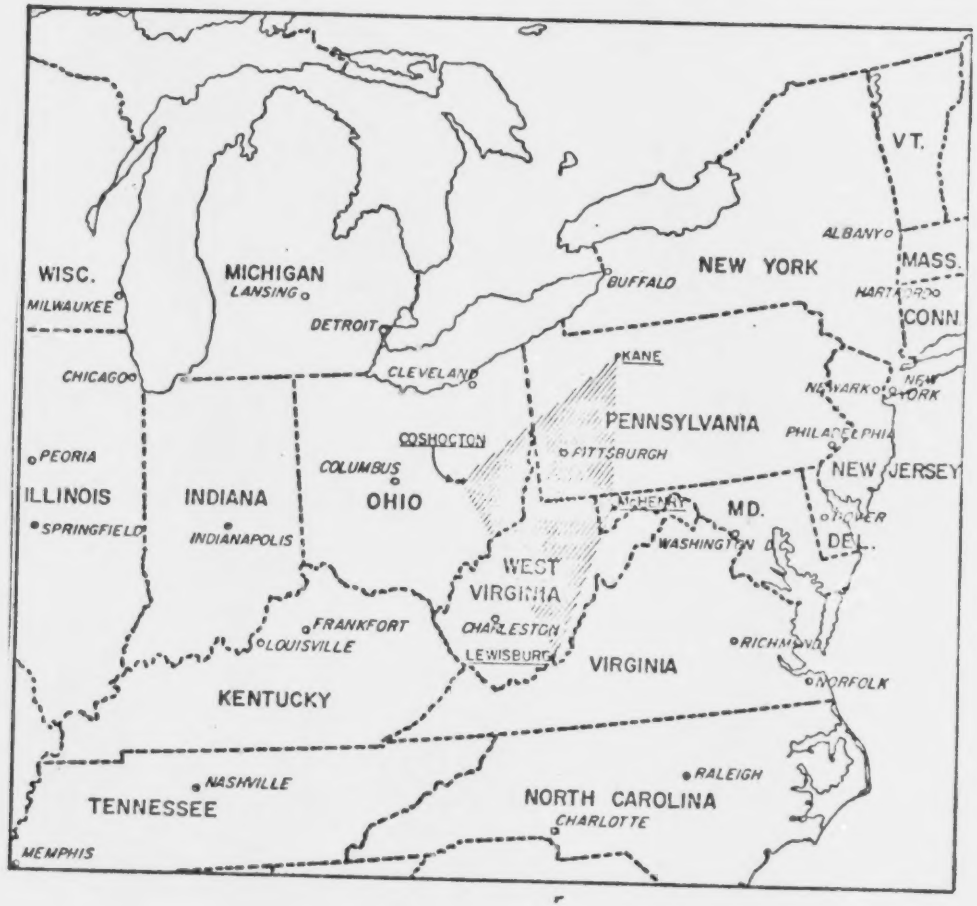

Figure 1. Rural oxidant study area.

Table 1. SUMMARY OF POLLUTANT CONCENTRATIONS, 6/26/73 TO 9/30/73

	McHENRY	KANE	COSHOCTON	LEWISBURG
	(HOURLY OZONE CONCENTRATIONS)			
MEAN	149 $\mu g/m^3$	130 $\mu g/m^3$	112 $\mu g/m^3$	105 $\mu g/m^3$
MAX	330 $\mu g/m^3$	270 $\mu g/m^3$	340 $\mu g/m^3$	250 $\mu g/m^3$
STD. DEV.	56 $\mu g/m^3$	57 $\mu g/m^3$	63 $\mu g/m^3$	54 $\mu g/m^3$
CASE COUNT	1,622	2,131	1,785	1,663

	(HOURLY NITROGEN DIOXIDE CONCENTRATIONS)			
MEAN	———	11 $\mu g/m^3$	21 $\mu g/m^3$	16 $\mu g/m^3$
MAX	———	40 $\mu g/m^3$	70 $\mu g/m^3$	60 $\mu g/m^3$
STD. DEV.	———	8 $\mu g/m^3$	15 $\mu g/m^3$	15 $\mu g/m^3$
CASE COUNT	———	1,869	2,043	1,699

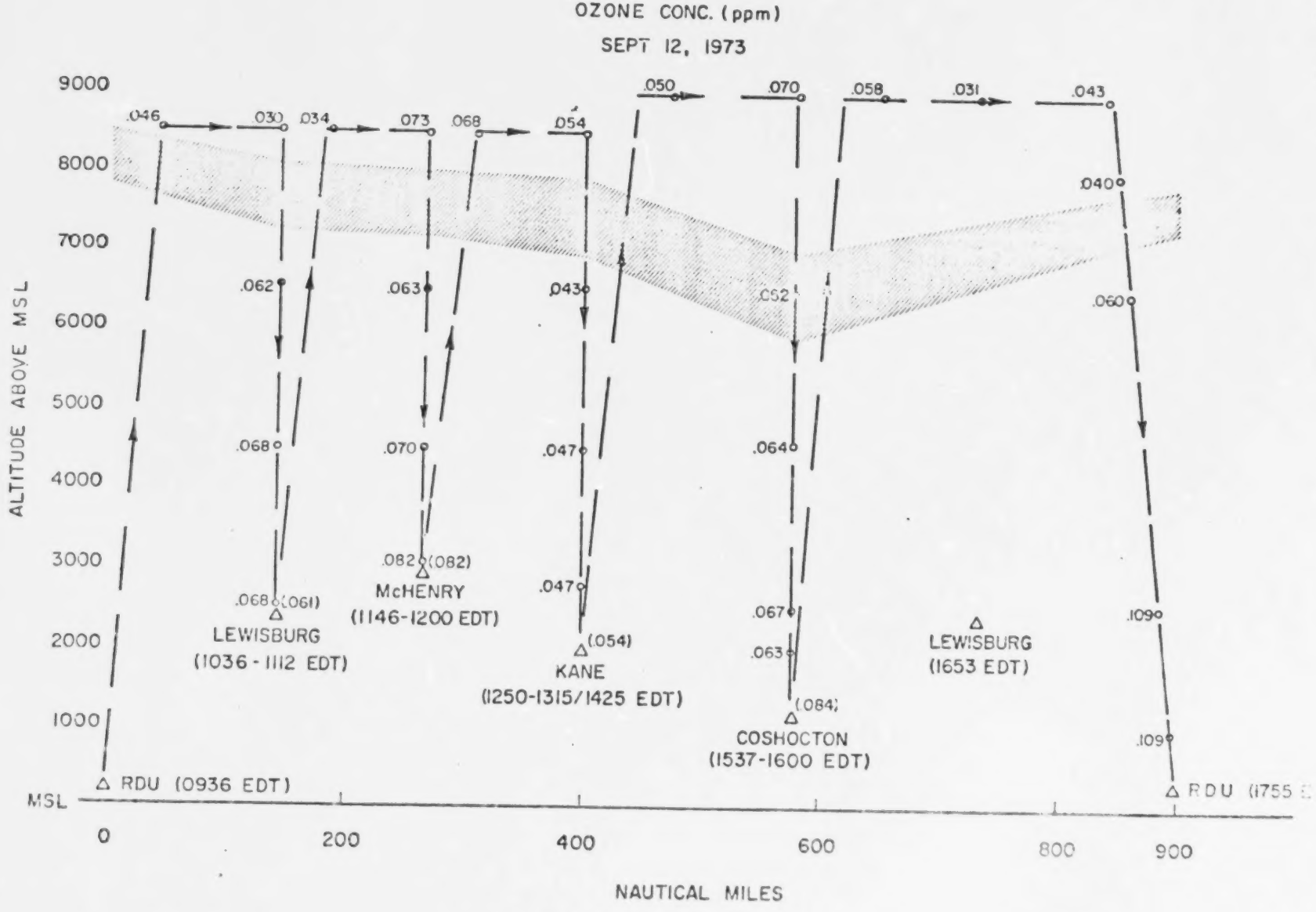

Figure 2. Ozone aircraft measurement

Table 2. RURAL OZONE STUDY

Station	Oxidant Concentrations		
	Max. Value	99%	% of time Above Stds.
McHenry	0.18	0.16	78
Kane	0.15	0.13	65
Coshocton	0.18	0.17	46
Lewisburg	0.13	0.12	39

Table 3. ESTIMATED HYDROCARBON EMISSIONS
(1000 tons/year)

AQCR	Mobile		Stationary	
	1970	1990	1970	1990
Los Angeles	829	133	339	593
San Francisco	372	57	257	400
Houston	326	48	274	407
New York	1160	166	361	342
Washington, D.C.	221	40	47	98
Beaumont	69	10	152	157
Phoenix-Tucson	117	24	85	174

Table 4. HYDROCARBON EMISSION DISTRIBUTION

AQCR Year	Percent of Hydrocarbon Emissions	
	Mobile	Stationary
Los Angeles		
1970	71	29
1990	18	82
San Francisco		
1970	59	41
1990	12	88
Houston		
1970	54	46
1990	11	89
New York		
1970	76	24
1990	33	67
Washington, DC		
1970	82	18
1990	29	71
Beaumont		
1970	31	69
1990	6	94
Phoenix-Tucson		
1970	58	42
1990	12	88

4. The Concept of Reactivity and Its Possible Applications in Control -- B. Dimitriades, EPA

The concept of reactivity has been around for several years and discussions of its definition, significance, application, etc. have been presented in a number of published reports. Of this elementary information, three facts or premises need to be stressed here:

1. Of the several reactivity manifestations caused by organic pollutants, only one is of direct interest here: The one responsible for the maximum oxidant levels found in the atmosphere.

2. The reactivities of organics can be measured only by laboratory techniques (smog chambers); atmospheric data analysis offers no promise.

3. Organic emissions differ widely in reactivity.

Because these premises are crucial to the follow-up treatment of the subject, they will be discussed here in some detail.

The first premise has perhaps obvious validity, considering that oxidant is the only photochemical pollutant for which there is an air quality standard, and for which the designated abatement approach is based on control of organic emissions only. Nevertheless, two points must be stressed here:

(a) While the linkage of the organic emissions with the oxidant problem is used as the basis for deriving numerical control requirements, this linkage in itself is not the only reason for wanting to control organic emissions. It is certain that control of organic emissions will result in reduction not only of oxidant but also of other photochemical smog symptoms. This comment is made because there have been attempts made to degrade the need for HC control by questioning the validity of the oxidant standard.

(b) Reactivity has been defined in terms of the max. 1-hour concentration of oxidant observed during the 6-hour smog chamber test. This "max-1-hour-concentration" definition was adopted simply because the same definition is used for the air quality standard for oxidant. However, this does not mean that this is the only acceptable definition. For the purpose of defining and expressing the reactivity of an organic, one can use any kinetic or concentration entity that can be measured in smog chamber test, and that can be shown to relate quantitatively to the maximum oxidant concentration.

The second premise (that reactivity can be measured only by smog chamber techniques) is an obvious one. It is also an important one to keep in mind for the following reasons. In some applications, the limitations of the smog chamber techniques are prohibitive only because there exists an alternative, superior method. This is, for example, the case with the study of the oxidant-precursor relationships; in such study the aerometric data analysis method is more valid than

the smog chamber method. However, in the case of reactivity measurement, the limitations of the smog chamber method are not necessarily prohibitive; such limitations should be judged bearing in mind that the smog chamber method is the only alternative available.

The third premise (that organics differ widely in reactivity) is one the validity of which could be challenged, as explained next. In past and present practices, the maximum-oxidant reactivity of an organic is measured by irradiating for 6 hours in a smog chamber pure air containing prescribed levels of the test organic and NO. Oxidant begins to form and accumulate only after all of the NO has been oxidized into NO_2. Within this fixed 6-hour period then, organics which convert the NO into NO_2 very slowly, do not necessarily yield all the oxidant they can yield. They could yield their maximum oxidant concentrations if test conditions were different, e.g., if they were irradiated for longer than 6 hours. Therefore one could speculate that under prolonged irradiation conditions, as e.g. in transported city air, all but very few organics might manifest similar reactivities, rather than a wide range--and this of course would question the utility of the reactivity concept.

So, there <u>are</u> questions that challenge the validity of the third premise. Nevertheless, the existing evidence, although it raises questions, clearly does not invalidate the premise. Under conditions prevailing within an urban area--where the problem really is--the existing reactivity data certainly have some validity. Under transport conditions, i.e., under prolonged irradiation, some thought-to-be unreactive organics may exhibit higher reactivity, but there is no reason to believe that the reactivity range within the reactive organics should shrink drastically--at least, this is not what existing knowledge on reaction mechanism suggests.

Reactivity Classification of Organics

In an EPA effort to classify organics into reactivity classes, the main body of data used was obtained from three studies: the Battelle, the Shell, and the SRI reactivity studies. Data were also taken from other studies--HEW, BuMines, General Motors and Los Angeles County. Since these studies used different smog chambers and conditions, all reactivity data were expressed in terms of toluene equivalents, in the hope that this would permit pooling of data from all studies. However, despite this normalization, the reactivity values still differed considerably from study to study. For this reason, the classification was done separately for each of the three sets of data--Battelle, Shell, SRI--and results were combined subsequently.

Examination of the data suggested that the organics tested could be classified within 5 classes, as shown in Table 5. The 5-group classification was dictated by the degree of agreement among the three studies. Better agreement would have permitted classification into more than 5 groups; worse agreement would have the opposite effect. The degree of agreement varied. Thus, the Battelle and Shell studies correlated well, Whereas the correlations

with the Battelle and the Shell data were poor. This poor correlation of the SRI data with the other data prompted some of the reviewers of this EPA study to recommend that the SRI data not be included in the reactivity classification work. While such a recommendation has its merit, one must also consider that:

(a) the poor correlations between SRI and Battelle and Shell may reflect mostly the small number of correlation points;

(b) the SRI show good internal consistency;

(c) if the number of reactivity classes is reduced to 5 (and even better to 3) the disagreement of the SRI set with the other sets of data does not cause prohibitive problems; and

(d) the SRI study provides data for several organics not tested by others (Table 5). In conclusion, while the question of the SRI data inclusion is an open one, it was nevertheless decided to proceed with this first effort to do the reactivity classification, including the SRI data. Results are shown in Table 6. The only inconsistencies in this classification are caused by the data on isopropyl alcohol and i-butyl acetate. The Battelle data for these two organics suggest a Class-I classification, whereas the SRI and Shell data suggest classification in higher classes.

Based on the numerical ratings shown in Table 6, overall numerical ratings were derived for the 5 classes and are shown in Table 7. Class I is meant to include those organics that can be exempted from control.

Application of Reactivity Criteria in Control

There are two approaches to emission control:

(a) The "air quality management approach"

(b) The "best practicable means" approach

By the air quality management approach, control requirements are determined so as to achieve the air quality standards without considering availability or cost of control technology. The "best practicable means" approach requires emissions to be controlled to a level that is technically and economically feasible. Thus, the "air quality management" approach has a more rational basis but it may not be feasible; whereas the "best means" approach is feasible but it may not achieve the desired air quality improvement. Obviously a combination of the two approaches is also possible, perhaps with advantage, as described next.

First, the overall percent reduction (of ambient organics) required should be calculated using either EPA's Appendix J (Federal

Register, Aug. 14, 1971) or another method. Then, rather than controlling all emission sources uniformly, each emission source is controlled to a different degree as shown in equation (1):

$$(1-b)r_{total}(Source)_{total}=(1-b_1)r_1(Source)_1 + ... + (1-b_i)r_i(Source)_i \qquad (1)$$

where b_i designates the degree of control to be applied on the respective source; r_i is the reactivity of the emission mixture from each source; $(Source)_i$ designates emission rate; and b is the required degree of control, as calculated from Appendix J. Such b_i is to be a function of three things: (a) Reactivity of emission mixture from repsective source; (b) relative contribution to total emissions load; and (c) control technology available. [Note: Whereas b_i depends on reactivity of emissions before control was applied, r_i represents reactivity of emission left uncontrolled]. Thus, several sets of b_i-values could be developed, depending on the circumstances in the control region. The only requirement that must be met is that the set of b_i-values should be such that equation (1) is satisfied. How one goes about determining the optimum set of b_i-values is an open question at this time. In a first effort to answer this question EPA has awarded a contract to conduct a case study using as the case site the Southern California air basin. The contractor will gather inventory data and will attempt to develop a set of b_i-values, taking into consideration the three pertinent factors mentioned: reactivity, relative strength, and control technology available. Needless to say, the main objective in this study is not to develop reactivity-related emission standards. Rather, it is hoped that by going through this exercise of developing reactivity-related standards, the feasibility and merits of such standards will be explored and unforeseen problems will be identified.

Question-Problems in Application of Reactivity Criteria in Control

The fundamental questions to be asked here are whether a rigorous and systematic application of reactivity criteria in control is feasible and whether it really and truly has an advantage over the control regulations now in use. The answer to these questions would depend on the answers to three other questions:

(1) Are the inventory data available sufficiently detailed to permit a reactivity assessment of the emission mixtures from the various sources? Reactivities of emission mixtures cannot be estimated unless the mixture composition is known.

2) Assuming emission composition is known, how accurate is the calculation of mixture reactivity from mixture composition?

(3) In the event that application of reactivity criteria will require different degrees of control upon the various sources than now required, what would the benefit from such change be?

Question (1)--on detail of inventory data available--cannot be answered reliably at this time. While the data available may not be sufficiently detailed to permit application of the 5-group reactivity classification scheme, they may be adequate for use of the 2-group classification. We expect to have an answer to this question in the near future, as a result of a contract effort--an effort directly addressed to the sufficiency of the inventory data available.

Question (2)--on the accuracy of the reactivity calculations--cannot be answered precisely at this time. Present practice is to calculate the reactivity of a mixture from component mole fractions and component reactivities using the linear summation method. It is submitted here that the error in such calculations cannot be prohibitively large. Organics range in reactivity by more than an order of magnitude; the calculation error certainly is much less than that. Nevertheless, EPA is currently studying this question; there is an on-going modest effort to use photochemical modeling techniques to calculate mixture reactivity from individual component data.

Question (3)--on the benefit to be derived from application of reactivity criteria--cannot be answered now. However, an answer may be had in the next few months, as a result of an on-going EPA-contract effort on this subject.

All in all, it appears that the uncertainties concerning benefits and the problems in applying reactivity criteria in control depend on how rigorously or with how much detail these reactivity criteria are to be applied.

Discussion

Questions were raised in regard to the Appendix J curve which was referred to in Dr. Dimitriades' presentation. Dr. Dimitriades responded that this is a curve published in Federal Register issue of August 14, 1971, and is a guideline to calculate the hydrocarbon control required to reduce oxidant.

In response to other questions, Dr. Dimitriades indicated that the reactivity data available for the various organics, represent the ability of the organic to produce oxidant on a mole basis rather than on a weight basis. In response to whether this might create a bias toward a heavier weight compound, Dr. Dimitriades suggested that he didn't believe so. This problem, if indeed, present, could be solved relatively simply through numerical calculations.

Ms. Brunelle from Los Angeles County asked how strongly would EPA feel about the use of oxidant alone as the basis for reactivity. Dr. Dimitriades responded that there is no other choice at present since the oxidant problem alone provides the legal basis for hydrocarbon control.

In response to other questions Dr. Dimitriades indicated that the newly suggested reactivity classification of organics will be included in the proceedings from this conference.

Dr. Dimitriades also discussed the EPA contract effort to explore the development and use of reactivity criteria in control. Mr. Malkin asked whether in this contract there will be a complete inventory of the "benefits" to be obtained as a result of the use of such criteria. Dr. Dimitriades responded that the only benefit considered in the contract study is the oxidant reduction itself. In the discussion that followed, Mr. Malkin clarified that he meant to ask whether there were indeed benefits in terms of health effects as a result of the oxidant reduction. Dr. Altshuller responded that there is evidence that ozone indeed exerts health effects. Mr. Malkin objected to that and he made reference to an EPA study cited in the report "Environmental Quality - 1974" (by Council on Environmental Quality) in which the cost of health damage by oxidant/O_3 was given a zero dollar-value. Dr. Altshuller agreed that this seemed to contradict the very bases of the air quality standard for oxidant/O_3, but he insisted that regardless of the dollar-value given to health damage by oxidant, the evidence of oxidant-induced health effects was sufficiently compelling to lead to the development of a health related air quality standard for oxidant.

Table 5. REACTIVITY CLASSIFICATION OF ORGANICS

CLASS I (Nonreactive)	CLASS II (Reactive)	CLASS III (Reactive)	CLASS IV (Reactive)	CLASS V (Reactive)
C_1-C_3 paraffins	Mono-tertiary-alkyl benzenes	C_{4+}-paraffins	Primary- & secondary-alkyl benzenes	Aliphatic olefins
Acetylene	Cyclic ketones	Cycloparaffins	Dialkyl benzenes	α-methyl styrene
Benzene	Tertiary-alkyl acetates	Styrene	Branched alkyl ketones	Aliphatic aldehydes
Benzaldehyde	2-nitropropane	n-alkyl ketones	Primary- & secondary-alkyl alcohols*	Tri-& tetra-alkyl benzenes
Acetone		Primary- & Secondary-alkyl acetates	Cellosolve acetate	Unsaturated ketones
Methanol		N-methyl pyrrolidone	Partially halogenated olefins *	Diacetone alcohol
Tertiary-alkyl alchols		N,N-dimethyl acetamide		Ethers
Phenyl acetate		Partially halogenated paraffins*		Cellosolves
Methyl benzoate				
Ethyl amines				
Dimethyl formamide				
Perhalogenated hydrocarbons *				

* Tested by SRI only.

Table 6. SUMMARIZED REACTIVITIES AND CLASSIFICATION OF SOLVENTS

Solvent	Reactivity, Toluene Equivalents: Battelle Range	Battelle Avg	SRI Range	SRI Avg	Shell Range	Shell Avg	Class
Paraffins (including cycloparaffins)	0.4-0.6	0.5	0.9-0.9	0.9	0.8-1.0	0.9	III
Olefins							
Aliphatic	1.3-1.5	1.4	-	-	1.8-3.1	2.4	V
Styrene	0.7	0.7	-	-	-	-	III
α-methyl-Styrene	1.5	1.5	-	-	-	-	V
Aromatics							
Benzene	0	0		-	0.2	0.2	I
Primary-, secondary-Alkyl Benzenes	0.9-1.2	1.0	1.0	1.0	1.0-1.2	1.1	IV
Tertiary-Alkyl Benzenes	0.6	0.6	-	-	0.5-0.5	0.5	II
Dialkyl-Benzenes	1.0	1.0	-	-	1.3-1.7	1.5	IV
Tri-, tetraalkyl Benzenes	1.5	1.5	-	-	3.2	3.2	V
Ketones							
Acetone	0	0	-	-	0.1	0.1	I
n-Alkyl Ketones	0.5-0.8	0.65	0.9	0.9	0.9-1.4	1.1	III
Branched Alkyl Ketones	1.0-1.8	1.4	0.9-1.0	0.95	1.3	1.3	IV
Cyclic Ketones	0.2	0.2	0.5	0.5	0.5-0.6	0.5	II
Unsaturated Ketones	1.5-1.7	1.6	-	-	-	-	V
Alcohols							
Methanol							I
Primary-, secondary-Alkyl Alcohols (C>1)	0.2	0.2	1.1-1.2	1.2	0.6-1.45	1.1	IV
tertiary-Alkyl Alcohols	-	-	-	-	0.3	0.3	I
Diacetone Alcohol	1.4	1.4	1.7	1.7	-	-	V
Ethers							
Diethyl Ether	-	-	-	-	2.5	2.5	V
Tetrahydrofuran	1.9	1.9	-	-	1.4	1.4	V
Ethyl Cellosolves	1.5	1.5	1.9	1.9	-	-	V
Esters							
Primary-, secondary-Alkyl Acetates	0.2	0.2	0.7-1.4	1.0	0.8-1.0	0.9	III
Tertiary-Alkyl Acetates	-	-	-	-	0.5	0.5	II
Cellosolve Acetate	-	-	1.1	1.1	-	-	IV
Phenyl Acetate	0	0	-	-	-	-	I
Methyl Benzoate	0	0	-	-	-	-	I

Table 6 (continued). SUMMARIZED REACTIVITIES AND CLASSIFICATION OF SOLVENTS

Solvents	Reactivity, Toluene Equivalents						
	Batelle		SRI		Shell		
	Range	Avg	Range	Avg	Range	Avg	Class
Amines							
Ethyl Amines	0.1-0.2	0.15	-	-	-	-	I
N-Methyl-Pyrrolidone	0.7	0.7	-	-	-	-	III
N,N-dimethyl-Formamide	-	-	-	-	0.2	0.2	I
N,N-dimethyl-Acetamide	-	-	-	-	0.95	0.95	III
Halocarbons							
Perhalogenated	-	-	0.5-0.5	0.5	-	-	II
Partially Halogenated Paraffins	-	-	0.8	0.8	-	-	III
Partially Halogenated Olefins	-	-	1.4	1.4	-	-	IV
Nitroalkanes							
2-Nitropropane	0.2	0.2	0.7	0.7	-	-	II

Table 7. NUMERICAL ACTIVITY RATING
IN THE 5-CLASS CLASSIFICATION OF ORGANICS

Class	Rating
I	1.0
II	3.5
II	3.5
III	6.5
IV	9.7
V	14.3

5. EPA Critique of Rule 66 and Appendix B -- F. Porter, EPA

Most overall emission control strategies which have been advanced to reduce ambient atmospheric levels of photochemical oxidants are based on either a "Rule 66" approach or an "Appendix B" approach. A "Rule 66" approach recognizes to some extent the wide variation in "reactivity" of various classes of hydrocarbons. The primary emphasis of a "Rule 66" approach is to limit the emission of a few hydrocarbons (of high reactivity) much more severely than the emissions of most hydrocarbons (of low reactivity). Thus, this approach concentrates more on changing the character of hydrocarbon emissions rather than reducing emissions and is based on the premise that hydrocarbons of low reactivity do not significantly contribute to the formation of photochemical oxidants.

An "Appendix B" approach on the other hand tends to overlook the wide variation in reactivity of various classes of hydrocarbons. The primary emphasis of an "Appendix B" approach is to severely limit the emission of all but a few hydrocarbons into the atmosphere. This approach is based on the premise that all hydrocarbons, whether of high or low reactivity, will contribute to the formation of photochemical oxidants over a long time period.

"Rule 66" was developed and initially implemented by the LAC-APCD in mid-1966 and subsequently amended in late 1971 and late 1972. The adoption of "Rule 66" by the LAC-APCD represented a major effort to reduce the formation of photochemical smog by reducing emissions of nydrocarbons. Throughout the development of "Rule 66", the LAC-APCD consulted closely with many of the industries affected by these regulations and as a result, although many of the industries questioned the need and desirability of "Rule 66", it was ultimately accepted as a "workable" and feasible approach to reduce the formation of photochemical smog. Currently, the "Rule 66" approach has been adopted in one form or another, as the basis for that portion of the State Implementation Plan dealing with the attainment and maintenance of the National Ambient Air Quality Standards for Photochemical Oxidants, in some twelve states.

"Appendix B" was developed by EPA and promulgated in August 1971, as part of the Requirements for Preparation, Adoption and Submittal of Implementation Plans in Federal Register 36 FR 15486. "Appendix B" reviewed the degree of emission control which could be attained with regard to specific air pollutants emitted from various industrial sources. The emission limitations presented, represented at that time EPA's judgment of the degree of emission control which could be attained with reasonably available emission control technology. The intention of EPA was not to require or encourage states to adopt "Appendix B"

but to provide a general base of knowledge with regard to the extent by which emissions could be reduced from various industrial sources. Thus, the intention of EPA was that the knowledge provided by "Appendix B" would serve as a general background against which states could make emissions control decisions and develop emission regulations for inclusion in their Implementation Plans, tailored to their specific problems and needs. Currently, the "Appendix B" approach has been adopted in one form or another, as the basis for Implementation Plans submitted to EPA, by some twenty-seven states.

Both "Rule 66" and "Appendix B" therefore serve as the basis for a number of State Implementation Plans. In this regard, both approaches will be implemented to various degrees in a number of states as a means of reducing and controlling ambient concentration levels of photochemical oxidants in the near future.

In any critical review of the effectiveness of a "Rule 66" or an "Appendix B" approach to reducing and controlling the formation of photochemical oxidants, the major conclusion that emerges is that neither approach by itself can be judged to be totally effective at this time. A "Rule 66" approach, as exemplified by the regulations currently in effect in Los Angeles County, represent a rather sophisticated approach. The wide variation in reactivity of various classes of hydrocarbons is recognized to some extent; the possible increase in reactivity of hydrocarbons under adverse processing conditions such as incomplete combustion and the general undesirability of permitting uncontrolled emissions of hydrocarbons of low reactivity from very large emission sources, one recognized to some extent. In addition, the recent and continuing development of new technology in the area of surface coatings such as water-based, high-solids and powder coatings, is encourgaed to some extent.

Even in its most sophisticated form, however, as mentioned earlier, the primary emphasis of a "Rule 66" approach is to limit the emissions of hydrocarbons of high reactivity much more severely than the emission of hydrocarbons of low reactivity, thus concentrating more on changing the character of the emissions, rather than reducing them. The ultimate ambient concentration levels of photochemical oxidants, which are eventually reached in a local area over a period of time, depends on their accumulation. This however, depends on a number of interrelated, competing and complex mechanisms, many of which are not well understood. Generally, it would appear that hydrocarbons of low reactivity permit a number of factors which tend to decrease the accumulation of oxidants in a local area, such as internal-mixing and dispersion within the local atmosphere and transport by favorable meterological conditions from the local area, to take effect to some extent. Thus, in specific areas, under favorable topographical and meteorological conditions, this approach could be an effective means for reducing local ambient concentration levels of photochemical oxidants. In many other areas however, this approach could be completely ineffective and all hydrocarbons emitted into the atmosphere could be expected to contribute to local concentration levels of oxidants.

To the extent that a "Rule 66" approach can be credited with reduction or control of local ambient concentration levels of photochemical oxidants in the immediate area in which this approach is implemented is, of course, consistent with the overall goal on the national level of reduced ambient concentration levels of photochemical oxidants. However, in judging the effectiveness of a "Rule 66" approach at the national level, consideration must be given to the effect of this approach on area-wide ambient concentration levels of oxidants, in addition to the effect on local concentration levels. A low reactivity rating does not necessarily mean that a particular hydrocarbon does not contribute to the formation of photochemical oxidants. If hydrocarbons of low reactivity contribute little to local photochemical oxidant formation, as a result of transport from the immediate area by favorable meteorological conditions for example, this implies that they may contribute to local oxidant formation in other areas. The extent to which this phenomena might lead to high ambient concentration levels of oxidants in surrounding local areas, would depend on a number of complex factors, among them, the degree of dispersion among these areas and the residence time in each.

Initial investigations into the effect of dispersion and transport of hydrocarbons and photochemical oxidants from local areas to surrounding areas, appears to indicate that this phenomenon can be a significant contributing factor to high local ambient concentration levels of oxidants in these surrounding areas. If a "Rule 66" approach were implemented in a particular area and this contributed to high local oxidant concentrations in surrounding areas, this would have to be viewed as an unacceptable approach, even if it lead to some reduction of local oxidants concentrations in the immediate area.

From an overall viewpoint therefore, while a "Rule 66" approach may be a very sophisticated approach in terms of recognizing a number of factors which bear on local ambient concentration levels of oxidants, it is based on the premise that hydrocarbons of low reactivity contribute little to local oxidant formation and that local oxidant formation is essentially a function only of local emissions of hydrocarbons. This fails to recognize that under many conditions, all hydrocarbon emissions could be expected to contribute to local oxidant formation. It also fails to recognize that the transport of hydrocarbons and oxidant from surrounding areas into local areas may be a significant factor contributing to high local oxidant concentration levels. In this case, the implementation of a "Rule 66" approach in surrounding areas could be expected to magnify the adverse effect of this transport phenomenon and could lead to higher local oxidant concentration levels.

An "Appendix B" approach to reducing and controlling the formation of photochemical oxidants, as exemplified by the August 1971 Federal Register, represents a rather pragmatic, if somewhat unsophisticated approach. Essentially, all hydrocarbon emissions are treated equally, in that the same degree of emission reduction is required irrespective of the relative reactivities of various classes of hydrocarbons emissions.

In addition, little consideration or encouragement is given to the recent and continuing development of new technology in the area of surface coating such as water-based, high-solids and powder coatings.

The primary emphasis of an "Appendix B" approach, is to reduce all emissions of hydrocarbons to the greatest possible extent, through the use of readily available emission control technology. As mentioned earlier, the basic premise underlying this approach is that all hydrocarbons whether of high of low reactivity, will contribute to the formation of oxidants over a long time period. Consequently, while this approach may acknowledge that a few specific hydrocarbons are completely unreactive and that emissions of these hydrocarbons need not be reduced, given the fact that most hydrocarbons are reactive, the wide variation in reactivity of various hydrocarbons is of little importance. Thus, the basic premise of this approach treats all reactive hydrocarbons equally and leaves no options to relate emission reductions in some fashion to relative reactivities.

At the time "Appendix B" was formulated within EPA, the possibility that transport of oxidants and hydrocarbons from surrounding areas into local areas might be a significant factor contributing to high local ambient concentration levels of oxidant, was not recognized. Thus, "Appendix B" as "Rule 66", was developed on the premise that local ambient concentration levels of oxidants resulted from local emissions of hydrocarbons. The basic difference between these two appraoches being essentially that "Rule 66" considered hydrocarbon reactivity to be a significant factor bearing on the ultimate concentration levels of oxidants attained in a local area, whereas "Appendix B" considered this factor of less significance in view of the total quantities of hydrocarbons emitted into the local atmosphere.

In light of today's recognition of the possible adverse effects on local ambient concentration levels of oxidants, due to the phenomenon of transport of oxidants and hydrocarbons from surrounding areas into a local area, an "Appendix B" approach seems more suitable than a "Rule 66" approach for coping with this situation. Although conceptually "Appendix B" might appear to be the most desirable approach to follow, full implementation of this approach in all cases could present considerable difficulties.

Hydrocarbons are emitted from a vast number of sources, both in terms of number and physical variety. There is no single, universal emission control technique. Rather there are a number of differing emission control techniques that vary in their adequacy to limit emissions from source to source and from hydrocarbon to hydrocarbon. The closest technique to being universal is incineration. However, under todays' constraints of limited fuel availability and high fuel prices, it is likely that this emission control technique may only represent a viable, practical alternative if vast heat recovery and utilization is possible.

In the particular area of organic solvents and surface coatings, reformulation of coatings to water-based, high-solids or powder coatings appears to be a potentially useful technique to reduce emissions of hydrocarbons. Yet developments in this area appear to be embryonic in many cases and the specifications that many coatings must meet require extensive and time consuming test programs. Similar problems also appear to exist in many other areas and with many other emission control techniques.

In regard to full implementation of either a "Rule 66" approach, or an "Appendix B" approach, therefore, it appears that while an "Appendix B" approach might be more desirable conceptually, it could give use to a number of problems in specific situations. Implementation of a "Rule 66" approach on the other hand, would likely give rise to few problems since it has proven both generally acceptable to industry and "workable" over the past eight years in Los Angeles County. However, it should be noted that in some areas, a "Rule 66" approach might not result in a significant reduction in local ambient concentration levels of oxidants and might even result in significant increases in ambient concentration levels of oxidants in surrounding areas, due to transport of hydrocarbons and oxidants to these areas.

The EPA goal in this matter, of course, is to achieve significant reductions in ambient concentration levels of photochemical oxidants in order to achieve and maintain the National Ambient Air Quality Standards for Photochemical Oxidants throughout the United States. Long-range this appears to imply the need for a reduction in hydrocarbon emissions to the greatest extent possible. Consequently, an "Appendix B" approach to photochemical oxidants appears necessary over the long term to maintain the Ambient Air Quality Standards; although in a few specific, isolated areas, where transport phenomenon would not give rise to problems in other areas, a "Rule 66" approach might prove adequate.

From an air pollution control viewpoint, it would be most desirable to implement an "Appendix B" approach as completely and as soon as possible. However, it appears that this course of action could give rise to a number of problems in specific situation. Consequently, over the short-range, while an "Appendix B" approach should be implemented as fully as possible, in those situations where the implementation of an "Appendix B" approach is not a viable alternative, a "Rule 66" approach should be implemented as an interim measure. However, adequate precautions should be incorporated in those areas where a "Rule 66" approach is implemented, to encourage and insure continued development of technology to accommodate the ultimate implementation of an "Appendix B" approach within a reasonable time frame.

Discussion

Comments from the floor suggested tha the EPA "Appendix B" is unreasonable in that, e.g , it does not exempt the unreactive acetone from control. Also questions were raised regarding the rationale of the Rule 66 restriction that organic emission from a single source should not exceed 3000 lb/day. While no answers were given to these questions, Ms. Brunnelle of LAAPCD stressed that the Rule 66 was intended for use in LA only and that the Rule sought to limit only those emissions that would cause a pollution problem only within LA. In questions regarding the utility of diffusion models in predicting pollutant dispersion, Mr. Neligan responded that the models now in use are applicable for dispersion distances no longer than 30-40 miles. Mr. Neligan further stressed that one does not need a diffusion model to see that pollutants are being transported; if a model does not predict such transport, then something must be wrong with the model.

Mr. Zimmt (NPCA) commented that the repeatedly made statement that "the organic pollutants that survive the within-city irradiation will react after they are swept out of the city" is only speculation. Mr. Zimmt also offered the National Paints and Coatings Association viewpoint on the discussion subject, summarized as follows:

"There are three parts to the emissions control problem:

(1) Need for emissions reduction

(2) Viable control techniques

(3) Reasonable compliance schedule.

Some parts of the country have adopted Rule 66 when there was no demonstrated need for emissions reduction and when viable control techniques were not available.

NPCA endorses Rule 66 as an inducement to develop new "low emissions" coatings. Solvent removal by treatment is technically and financially not feasible.

NPCA suggests switching to low reactivity solvents until new solvents or techniques are ready."

Questions were also asked about EPA's efforts, if any, to identify non-photochemical sinks of organic pollutants. Dr. Dimitriades responded that while there are several EPA studies on fate of pollutants, he was not aware of any studies specific for HC. He added that if such sinks exist, to all probability, they would reduce only the long term effects of the organic emissions; there are no indications that urban emissions, while within the urban area, would be appreciably affected by such sinks.

AFTERNOON SESSION

1. Reactivity Classification of Organics -- A. Levy, Battelle-Columbus

A number of solvent reactivity studies were reviewed mainly with the intent of examining strengths and weaknesses in reactivity classification. First, consideration is given to the use of reactivity as a control procedure relative to total reduction of organic emissions. Consideration is then given to the various definitions of reactivity, with special attention as to how the various reactivities relate to one another. Detailed examinationwas then made of oxidant reactivity data from several programs. It is shown that when HC/NO_x ratios are comparable oxidant reactivity is also comparable, even when absolute concentration levels are varied. Correlation analyses also compare favorably under similar chamber conditions. Special attention is directed to the importance of background mixtures in evaluating reactivity, especially in bringing out the influence of synergistic effects in simple, binary solvent systems. It is on this basis that linear summation rules are examined and shown to be wanting. Lastly, some examples are presented which illustrate the pronounced effect of HC/NO_x ratio on reactivity. It is concluded that to be able to generalize solvent reactivity concepts, so they may be applied more broadly in terms of chemical structure, a more rigorous chamber procedure for evaluating solvents is needed.

Discussion

The question was asked whether synergistic effect would cause organic mixtures to manifest higher or lower reactivities than expected. Dr. Bufalini explained that the answer depends on the HC-to-NO_x ratio factor. If the HC-to-NO_x ratio is constant, then the synergism usually has a positive effect, i.e., a mixture of organics is more reactive than the individual component reactivities suggest. To the question whether this relates to need for NO_x control, Dr. Bufalini responded that NO_x control requirements are based on entirely different considerations.

In response to Mr. Romanovsky's inquiries, Mr. Levy stated that reactivity manifestations that do not correlate to oxidant yield are not of much interest at the present time. Mr. Romanovsky took exception to this viewpoint. He explained that organics should not be judged solely by their oxidant yields; rather, they should be judged by the degree to which they participate in atmospheric reactions since such participation will ultimately lead to formation of objectionable pollutants.

2. An Experimental Protocol For Reactivity Measurement -- C. W. Spicer, Battelle-Columbus

Many investigations have been carried out over the years on the photochemical smog reactivity of solvents and other organic materials. There has never been a consistent procedure, however, which attempts to maximize both the realism of the reactivity assessment and the efficiency of the operation. Thus, investigations have been carried out using a variety of experimental conditions which very likely affect the results of the study. Examples cited are variations in the initial organic to

nitrogen oxides ratio, the concentration or loading of the organic studied, and the effect of the presence of other hydrocarbons on the reactivity of the specie of interest. Discussion of these three variables is aimed at demonstrating their effect on organic reactivity and especially on realtive reactivity. The point of this part of the discussion is that future reactivity studies should consistently employ a known set of predetermined experimental conditions so that reactivity results are more directly comparable. The experimental conditions should be chosen so as to represent as closely as possible actual atmospheric reactivity conditions.

Due to the long list of organics which should be investigated in a future reactivity study, it is imperative that an efficient reactivity procedure be employed. A method whereby a large existing smog chamber is broken down into 4 to 5 smaller chambers through the use of Teflon compartments is discussed. Particular emphasis is placed on the efficiency of the operation, e.g., 4 or 5 simultaneous smog chamber experiments could be run in 1 day, and the low cost of implementing such a procedure. The chamber, light bank, and instrumentation would remain unchanged; the instruments would be automatically cycled among the Teflon compartments for maximum efficiency. The use of background mixtures in future reactivity studies will also be discussed and a specific replacement scheme will be suggested.

Discussion

Dr. Dimitriades asked for clarification regarding the reactant concentrations to be adopted in the reactivity measurement protocol. Dr. Spicer responded that reactant concentration conditions would be decided upon at a later time.

Mr. Zimmt (NPCA) inquired whether plastic film bags could be used as smog chambers. Mr. Levy responded that choice of wall material is dictated by wall effect considerations. In a generalized sense, small smog chambers cause wall effects that can in turn cause interferences, especially in photochemical aerosol studies. Dr. Dimitriades added that recent studies at Lockheed (under CRC-EPA contract) indicated that wall material and surface-to-volume ratio are smog chamber design parameters that affect smog chamber results significantly and that, therefore, they should be considered carefully in development of a reactivity measurement protocol.

3. Critique of Solvent Reactivity, Rule 66, and Appendix B -- W. L. Faith, Consulting Engineer

Dr. Faith agreed that a sound and definite regulation should be developed to control emissions of photochemically reactive compounds into the atmosphere. He further agreed that the amount of control should bear a reasonable relationship to the relative "reactivity" of the emitted organic compound. Dr. Faith stressed that organic vapors emitted not in mixture with NO_x do not pose a photochemical pollution problem. He also expressed his belief that control of stationary source emissions in Los Angeles did not prove to be of any benefit to local air quality. Dr. Faith proposed the following type of regulation:

"Emissions should be classified as follows:

1. High reactivity - organics mixed with NO_x in stated ratios prior to emission.

2. Moderate reactivity - all non-aromatics containing a carbon-carbon double bond, and all di-substituted and higher aromatics.

3. Low reactivity - all non-aromatics not containing a carbon-carbon double bond, and not in Class 4; toluene.

4. Negligible reactivity - compounds now in Appendix B.

"Within each class, degree of control should be related to volatility, e.g., (a) > 1 mm Hg, (b) 0.1 - 1 mm Hg, (c) 0.0 - 0.1 mm Hg, (d) < 0.01 mm Hg.

"Also control the emissions for a given evaporated solvent to a similar degree as other organic emissions.

"Set up a referee system and test protocol to establish relative reactivity of specifically questioned compounds and relate their relative reactivity to 2 or 3 standard compounds, e.g., propylene, toluene, and isopropyl alcohol."

Discussion

Mr. Neligan (EPA) took strong exception to Dr. Faith's contention that control of stationary source emission in LA during the late 1950's has been of no benefit to local air quality. Mr. Neligan explained that such a conclusion could hardly be substantiated in view of the fact that the emission increment caused by growth of both mobile and stationary sources had more than offset the decrement achieved by control.

Mr. Sussman (Ford) commented that based on existing regulations, one may conclude that only the 6-9 a.m. emissions need to be controlled (Mr. Sussman later in the session stated that his suggestion was facetiously offered). Dr. Dimitriades responded that such conclusion was based on misinterpreation of the regulations.

Dr. Dimitriades made reference to Dr. Faith's statement that organic emissions discharged without NO_x present no problems, and asked whether Dr. Faith shared the opinion voiced earlier in the session that the natural--rather than man-made--organic emissions may be largely responsible for the oxidant problem. Dr. Faith responded that the naturally emitted organics, in his judgment, are not part of the problem.

Questions were also addressed to the speaker regarding the role of NO_x and of pollutant transport in oxidant formation. Dr. Faith responded that NO_x--and not hydrocarbon--is the oxidant precursor that should have been controlled from the beginning of the control efforts. Further, he disagreed with Mr. Neligan's comment that a significant portion of the oxidant problem at Indio, California, is caused by Los Angeles emissions; he submitted that

the problem is caused by local emissions. Mr. Neligan said that the Palm Springs-Indio area was violating the oxidant standard more than twice as frequently as were stations in Los Angeles County according to CARB reports and the maximum values were approximately the same level. In addition, hydrocarbon emissions in Los Angeles County were about 15 times greater than in San Bernardino County, and 20 times greater than in Riverside County.

4. Development of a Study Program (Research Needs) -- A. Levy, Battelle-Columbus

Mr. Levy suggested a research program aimed at updating the current status of organic solvent reactivity. A prospectus was presented to the attendees outlining a proposed program. The program would have two principal objectives. The primary objective would be to evaluate and correlate the photochemical smog reactivity or organic solvents with chemical structure. A secondary objective would be to expand and broaden current knowledge on the influence of parameters on reactivity. In order for such a program to be of maximum value to both industry and government, it was suggested that a new reactivity procedure be developed for use in this new program. This new procedure would make it possible to evaluate a solvent under a variety of conditions by simultaneously carrying out the irradiation of several systems in a multi-chamber facility. This program would be operated through an Advisory Committee representing the sponsoring groups. The hope was also expressed the EPA would provide one or two people to serve in an ad hoc advisory capacity to this committee. The suggested program would be a two year program, starting about September 1974.

Discussion

Questions were asked from the floor regarding EPA's input to the design of the proposed program. It was specifically asked whether and how would EPA use the information output from this program. Dr. Dimitriades (EPA) responded that EPA cannot be expected to make any commitment regarding its future stand on the subject of reactivity. He stressed, however, that at present, EPA is actively interested in the concept and use of reactivity and will certainly pay close attention to the proposed effort and its findings. Responding further to questions from the floor, Dr. Dimitriades indicated that EPA will consider establishing formal liaison withthe planned activity and will make a decision shortly.

To other questions regarding specific objectives and scope of the contemplated study, Mr. Levy responded that such points would be discussed at a later time, after the general intent of the study and its desirability are established.

Mr. Zimmt suggested that the proposed study be designed so as to develop information relevant to the type of atmosphere expected at the time the study is to be completed. This led to questions regarding duration of proposed study; Mr. Levy indicated that he would recommend a program at least 2 years long.

SUMMARY-CONCLUSIONS

The concept of photochemical reactivity and its present use in solvent emissions control strategies was reexamined for validity, utility, and desirability. Such reexamination was instigated by a number of recent developments, including the following:

1. EPA realized that reactivity criteria are not used consistently in existing control regulations--such an inconsistency being, in principle at least, undesirable.

2. Recent smog chamber studies showed that some thought-to-be-unreactive organics are in actuality reactive--a reversal that invalidates the reactivity classification (of organics) in the widely used Los Angeles County Rule 66.

3. It has become increasingly evident that pollutant transport does occur, and that such transport enchances formation of oxidant from low reactivity organics.

4. EPA realized that the present emphasis on control of the mobile source emissions will eventually make solvents and the other stationary source emissions the predominant emission problem.

Except for one dissenting opinion, there was general agreement that control of solvent vapors and of other organic emissions from stationary sources is necessary, and that use of reactivity criteria on such control is, in principle, sound. The dissenting opinion was that solvent vapors, as well as any other organic emissions that are emitted unmixed with NO_x, do not pose a photochemical pollution problem.

In regard to use of reactivity criteria in control, EPA contended that present practices, as reflected in the predominantly used Los Angeles County "Rule 66" and EPA's "Appendix B" reactivity related guidelines, are not totally satisfactory. Thus, Rule 66 is lacking in two respects: First, its reactivity classification of organics is inaccurate, the error being in the direction toward less stringent control. Second, it assumes that organics of unknown reactivity are non-reactive--an assumption that is probably wrong and that again leads to less stringent control. Appendix B is lacking in that it assumes that all, except very few, organics are equally reactive--an assumption that is known to be wrong and that it causes inflexibility. Viewpoint from the solvents and paints manufacturers and users did not disagree with these contentions; however, it also emphasized that in the course of the years during which Rule 66 was the only reactivity related control regulations, manufacturing and trade practices have been shaped so as to make compliance with Rule 66 feasible. Further,

enforcement of an Appendix-B type new regulation, requiring drastic emission reduction by treatment, will incur serious economic penalties and, more importantly, will hamper development of other, environmentally much more advantageous products and processes, such as water-based and high-solids coatings.

Recent findings concerning occurence and effects of pollutant transport appear to provide additional support to the "all-organics" control concept advocated by Appendix B. Thus, under the prolonged irradiation conditions occurring in transported air masses, it is very probable that the "less reactive" organics are induced to form as much oxidant as the "more reactive" ones. Therefore, to alleviate oxidant problems both in the vicinity of the emission source and in the downwind areas, nearly universal control of organics, as prescribed by Appendix B, is more effective than the more selective control prescribed by Rule 66. In support of this conclusion, air pollution control officers from LA County stressed that Rule 66 was indeed conceived and designed to cope solely and specifically with the photochemical pollution problem within the LA air basin; no consideration was given to transport induced problems outside the basin. In view of these developments regarding pollutant transport, EPA is now inclinded to think that an "area-wide" approach to control may be advantageous over the "region-wide" approach now in use.

Regarding the need for more rigorous and consistent use of reactivity criteria in control, EPA offered some conceptual specifics on such use. Thus, it was suggested that control requirements for each source type should be calculated taking into consideration (a) the degree of total hydrocarbon control required for the region or area, (b) the relative strength of the source, (c) the reactivity of the emissions, and (d) the availability of control technology. EPA is not convinced that implementation of such an application of reactivity criteria is feasible at this time. Questions regarding the actual benefits from and problems in such application are still open, although they are being studied.

Finally, suggestions for future research needs were offered and discussed. EPA presented a new reactivity classification of organics, based on existing smog chamber reactivity data. It was agreed that reactivity data for additional organics are needed. It was further agreed, that research is needed to obtain more reliable techniques for calculating reactivities of emission mixtures.